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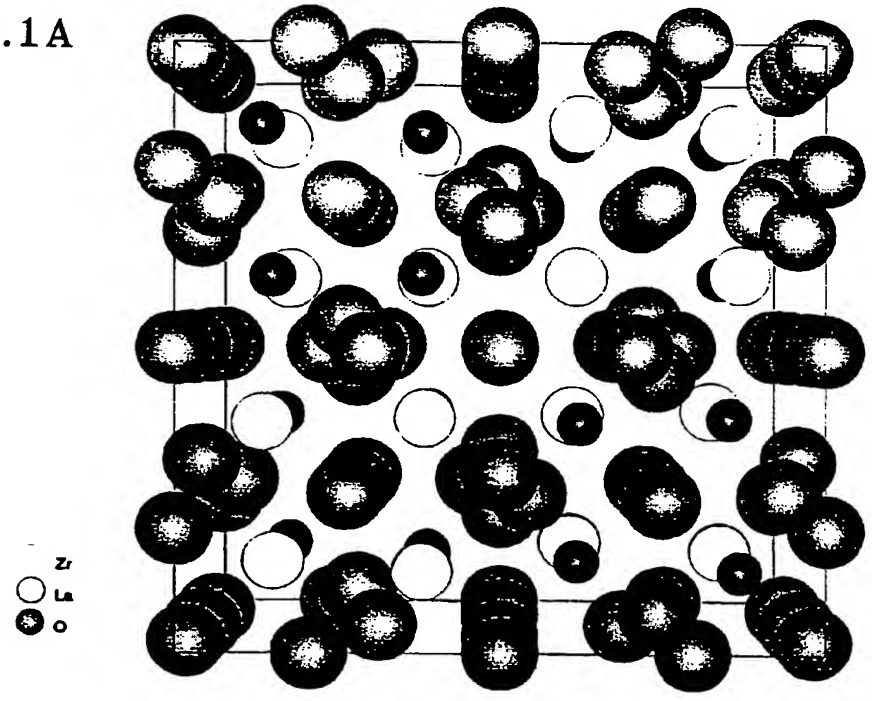
(54) Thermal barrier coating systems and materials

(57) A new family of ceramic materials is identified having particular utility as thermal insulating or thermal barrier coatings on metallic substrates. The ceramic materials have a pyrochlore structure and are typified by the composition $A_2B_2O_7$ where A and B are various ions and O is oxygen. A may have a positive charge of 3^+ or 2^+ and B may have a positive charge of 4^+ or 5^+. These materials are characterized by having chemical stability, thermal stability and thermal insulating properties superior to those of currently used thermal barrier ceramics. An example pyrochlore material is lanthanum zirconate.

FIG. 1A



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D scription

This invention relates to a class of ceramic materials for thermal barrier coatings, to thermal barrier coatings made of such materials, and to metallic parts having such thermal barrier coatings. The thermal barrier coatings have particular utility in gas turbine engines. The ceramic materials are a family of ceramics having a pyrochlore structure.

Gas turbine engines are well developed mechanisms for converting chemical potential energy, in the form of fuel, to thermal energy and then to mechanical energy for use in propelling aircraft, generating electric power, pumping fluids etc. At this time the major available avenue for improved efficiency of gas turbine engines appears to be the use of higher operating temperatures. However the metallic materials used in gas turbine engines are currently very near their upper limits of thermal stability. In the hottest portion of modern gas turbine engines, metallic materials are used at gas temperatures above their melting points. They survive because they are air cooled. But excessive air cooling reduces engine efficiency.

Accordingly, there has been extensive development of thermal barrier coatings for use with cooled gas turbine aircraft hardware. By using a thermal barrier coating, the amount of cooling air required can be substantially reduced.

Such coatings are invariably based on ceramics; mullite, alumina, etc. have been proposed but zirconia is the current material of choice. Zirconia must be modified with a stabilizer to preserve its cubic crystal structure at elevated temperatures, typical stabilizers include yttria, calcia, ceria and magnesia.

Generally speaking, metallic materials have coefficients ofthermal expansion which exceed those of ceramic materials, consequently one of the problems that must be addressed in the development of successful thermal barrier coatings is to match the coefficient of thermal expansion of the ceramic material to the metallic substrate so that upon heating, when the substrate expands, the ceramic coating material does not crack. Zirconia has a high coefficient of thermal expansion and this is a primary reason for the success of zirconia as a thermal barrier material on metallic substrates.

Thermal barrier coatings have been deposited by several techniques including thermal spraying (plasma, flame and HVOF), sputtering and electron beam physical vapor deposition (EBPVD). Of these techniques, electron beam physical vapor deposition is currently a preferred technique for demanding applications because it produces a uniqu coating structure. Electron beam physical vapor deposited ceramic materials, when applied according to certain parameters, have a columnar grain microstructure consisting of small columns separated by gaps which extend into the coating. These gaps allow substantial substrate expansion without coating cracking and/or spalling-see US patent 4,321,311. According to US patent 5,073,433 a similar structure (comprising segmentation cracks), although on a larger scale, can be obtained by plasma spray techniques.

Despite the success with the current use of electron beam physical vapor deposited zirconia base coatings there is a continuing desire for improved coatings which exhibit superior thermal insulation capabilities, especially improved insulation capabilities when normalized for coating density. Weight is always a critical factor when designing gas turbine engines, particularly in rotating parts. Ceramics thermal barrier coatings are not load supporting materials, consequently they add weight without increasing strength. There is a strong desire for a ceramic thermal barrier material which adds the minimum weight while providing the maximum thermal insulation capability. In addition there are obviously the normal desires for long life, stability, economy etc.

Although this coating was developed for application in gas turbine engines, the invention clearly has utility in other applications where high temperatures are encountered such as furnaces.

The essence of the present invention arises from the discovery that a class of ceramic materials has great utility as thermal barrier coatings on metallic substrates. These materials have a pyrochlore crystal structure.

Thus, viewed from a first aspect, the present invention provides a metallic article comprising a metallic substrate, said substrate having a ceramic coating on its surface wherein said ceramic coating has a cubic pyrochlore structure.

Viewed from a second aspect, the present invention provides a metallic article comprising a metallic substrate, said substrate having an alumina forming coating on its surface and a pyrochlore coating bonded to said alumina forming coating.

Viewed from a third aspect, tne present invention provides a method of thermally insulating a metallic substrate which comprises: applying a cubic pyrochlore ceramic coating to at least a portion of said substrate by electron beam physical vapor deposition, or by thermal spray deposition.

Viewed from a fourth aspect, the present invention provides that in a superalloy gas turbine component which operates in an environment with gas temperatures in excess of 1,000°C, said component having internal cooling passages, the improvement which comprises a coating of a ceramic having a pyrochlore crystal structure, said coating being located to reduce heat flow into said component.

Viewed from a fifth aspect, the present invention provides the use of a ceramic coating having a pyrochlore structure as a thermal barrier coating.

The term pyrochlore is used to identify an ore of tantalum found in Canada. The term more generally describes a ceramic structure of the composition $A_2B_2O_7$ where A can have valance of 3^+ or 2^+ and B can have a valanc of 4^+

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or 5^+ and wherein the sum of the A and B valences is 7. The oxygen can be replaced by in part by sulfur or fluorine. Typical pyrochlores which we believe to have potential as thermal barrier coatings are those in which A is selected from the group consisting of lanthanum, gadolinium and yttrium and mixtures thereof and B is selected from the group consisting of zirconium, hafnium and titanium and mixtures thereof. Many other pyrochlores exist which also have potential as thermal barrier materials. See "Oxide Pyrochlores - A Review" by M.A. Subramanian et al, Progress in Solid State Chemistry, vol 15, pp 55-143, 1983 (incorporated herein by reference) for a full description of pyrochlores.

We have found that on a density adjusted basis pyrochlores which we have investigated have thermal insulating properties which exceed those of the more commonly used zirconia based thermal barrier materials. Additionally many of the pyrochlore materials have a phase relationship in which the pyrochlore structure is phase stable up to the melting point. Consequently stabilizing additions are not required. Most of the pyrochlores which we have investigated have melting points of more than 3000°F (1650 °C) and generally more than 4000° F (2200 °C). Additionally these materials adhere to alumina. These are all properties which are useful in thermal barrier coatings.

The invention coating materials and coatings will usually be used to protect a superalloy substrate from excess temperatures. Superalloys are metals, usually based on iron, nickel or cobalt and containing chromium and aluminum and usually titanium and refractory metals, and having useful properties above 1200 °F (650 °C). Other substrates, including steels, copper alloys and titanium alloys may be protected. Table I describes exemplary substrate materials.

TABLE I

(wt % Exemplary Superalloy Compositions)														
	Cr	Co	W	Cb	Ti	Al	B	Hf	C	Ni	Ta	Mo	Zr	Re
PWA1422	9	10	12	1	2	5	.015	1.6	.14	Bal	-	-	-	-
PWA1426	6.4	12.6	6.4	-	-	5.9	0.012	1.5	-	Bal	3.0	1.7	.08	.3
PWA1480	10	5	4	-	1.5	5	-	-	-	Bal	12	-	-	-
IN 792	12	9	3.8	-	4.1	3.5	.015	0.5	.12	Bal	3.9	1.9	.12	-

As in other ceramic thermal barrier coatings, adherence of the pyrochlore ceramic to the alloy substrate is critical. It is known from prior zirconia thermal barrier coatings that a metallic bond coat (sometimes described as an overlay coating) such as a MCrAlY is a superior bond coat for oxide ceramic coatings. It is also known that aluminide coatings are useful bond coats through generally not as durable as MCrAlY bond coats. The common feature of overlay coatings and aluminide coatings is that they both form adherent alumina surface films or scales.

A broad composition range for MCrAlY materials is 10-25% Cr, 5-15 Al, .1-1.0 Y balance selected from Fe, Ni, and Co and mixtures of Ni and Co. Additions ofup to 5% each of Hf, Ta or Re, up to 1% of Si and up to 3% each of 0s, Pt, Pd, or Rh may also be made. Table II describes exemplary MCrAlYs that can be applied by thermal spray processes, by EBPVD processes, and by electroplating.

TABLE II

(wt % Exemplary MCrAlY Compositions)							
	Ni	Co	Cr	Al	Y	Hf	Si
MCrAlY	Bal	-	19.5	12. 5	.45	-	-
CoCrAly	-	Bal	18	11	.45	-	-
NiCoCrAlY	Bal	23	18	12.5	.3	-	-
NiCoCrAlY	Bal	22	17	12.5	.6	.25	.4

An alternate bond coat is a diffusion aluminide formed by diffusing aluminum into the substrate surface. Diffusion aluminides are well known and may be applied using a mixture (termed a pack) containing an aluminum source, such as an aluminum alloy or compound, an activator (usually a halide compound such as NaF) and an inert material such as alumina. The part to be coated is buried in the pack and heated to 1500-2000°F (816-1094°C) while a carrier gas, such as hydrogen, is flowed through the pack. Out of pack processes wherein the part is not buried in the pack are also known. The incorporation of precious metals such as Pt, Rh, Pd and Os into aluminide coatings is known. See US patent 5,514,482 for a description of aluminide coating processes.

Combinations of overlay and aluminide coatings are also possible. See US patent 4,897,315 for a description of a system having an inner MCrAlY overlay coating and an outer aluminide coating. See US patent 4,005,989 for a

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description of the reverse combination, an inner aluminide coating and an outer overlay coating.

The common feature of these bond coats and bond coat combinations is that they form an adherent layer of alumina on their outer surface. The invention thermal barrier coating has limited solubility in alumina but bonds firmly to the alumina.

In certain cases. superalloys may form sufficiently perfect and adherent alumina layers that ceramics may adhere without a separate bond coat. See US patents 5,262,245, 4,895,201, 5,034,284, 5,346,563, and 5,538,796.

To date all successful applications of ceramic coatings to superalloy has included oxide layer (usually alumina, rarely silica) between the bond coat (or substrate) and the ceramic coating.

Certain preferred embodiments will now be described by way of example only and with reference to the accompanying drawings, in which :

FIG. 1a depicts the crystal structure of lanthanum zirconate, a pyrochlore;
FIG. 1b depicts the crystal structure of zirconia, a fluorite structure;
FIG. 2 shows the relationship between the A and B constituent ionic sizes necessary to produce a pyrochlore structure;
FIG. 3a depicts a ceramic coating directly on a metallic substrate;
FIG. 3b depicts a ceramic coating on a metallic substrate with an intermediate bond coat;
FIG. 3c depicts an expanded view of the interface between the bond coat and the ceramic layer in FIG. 3b;
FIG. 4 shows the $Zr0_2$ - La_20_3 phase diagram;
FIG. 5 shows the thermal conductivity of several ceramic materials;
FIG. 6 shows the coefficient of thermal expansion for several ceramic materials; and
FIG. 7 shows an X-ray diffraction scan from the surface of a preferred coating.

The pyrochlore structure is a complex structure which can be described in a variety of ways, as a fluorite structure derivative, or as a network of octahedrals linked corner to corner with cations filling the interstices.

Fig. 1a is a depiction of a cubic pyrochlore crystal structure. Regardless of structure description the pyrochlor structure has a chemical composition of $A_2\ B_2\ 0_7$ or occasionally $A_2\ B_2\ 0_6$ or $AB_2\ 0_6$ with the latter two being referred to as defect pyrochlores. Fig. 1a illustrates lanthanum zirconate having an $A_2B_20_7$ chemistry. Fig. 1b shows a cubic fluorite structure, the structure of stabilized zirconia. A comparison of Figs. 1a and 1b shows both similarities and differences between the two structures. Both Figs. 1a and 1b are views down the <100> crystal axis. Visually the pyrochlore structure appears to be less regular than the fluorite structure.

The A and B ions can have different valances as long as the sum of the A and B valences adds up to 7, in the case of the A_2, $B_2\ 0_7$ or 6 in the case of $A_2B_20_6$ structures.

The pyrochlore structure forms only for certain relationships of A and B ionic radii. Fig. 2 illustrates this relationship indicating the general combination of A and B ionic radii which produce cubic pyrochlores. We have found that the boundaries of this diagram are somewhat uncertain and we believe, based on our investigations, that lanthanum titanate [$La_2\ Ti_2\ 0_7$] has a stable cubic pyrochlore structure.

Noncubic pyrochlores are known but for the purpose of this invention we prefer to use ceramics which have a cubic pyrochlore structure.

As shown in Fig. 2, the formation of the desired cubic pyrochlore crystal structure is controlled by the relative ionic radii of the A and B constituents. It is possible to use a mixture of elements for the A and/or B constituents to provide an average ionic radius which will cause formation of a cubic pyrochlore structure. By way of example, from Fig. 2 it can be seen that both $Gd_2Ti_20_7$ and $Y_2Zr_20_7$ will have cubic pyrochlore structures. As a general rule, compounds of the formula $(Gd_xY_y)(Ti_aZr_b)\ 07$, where x+y = 2 and a+b = 2, will also have a cubic pyrochlore structure.

Further, a compound such as $In_2Zr_20_7$ which is not cubic could likely be rendered cubic through partial substitution of (for example) Nd for In and/or Ti for Zr, to bring the average A and B ionic radii into the cubic pyrochlore region shown in Fig. 2.

We have worked with the type of pyrochlores denoted by the $A_2\ B_2\ 0_7$ formula and of these we prefer to use gadolinium, lanthanum or yttrium for the A ionic species and hafnium, titanium or zirconium for the B ionic species. Lanthanum zirconate seems particularly useful because lanthanum and zirconium have similar vapor pressures, making vapor deposition more readily possible. We have used only the materials of the $A_2\ B_2\ 0_7$ structure and have not attempted the use of the known pyrochlores which have either fluorine or sulfur to substitute a portion of the oxygen but we do not believe that there is any reason to exclude the sulfur and fluorine substituted compositions from the present invention. We have also not experimentally evaluated the $A_2B_20_6$ and AB_20_6 structures but believe that they also may have utility in thermal barrier coatings.

Ti, Zr and Hf all display complete solid solubility in each other and we believe that any combination of Ti + Zr + Hf can be used as the B ionic species. Similarly, Gd, La and Y have substantial solid solubilities (Gd - La has complete solubility). Any combination of Gd + La + Y which does not form a second phase can be used as the A ionic species.

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These alloys ofthe A and B species must satisfy the criteria of Fig. 2 and possess a pyrochlore structure.

The low thermal conductivity of oxide pyrochlore compounds can be rationalized by consideration of crystallographic and chemical effects on thermal conductivity. The thermal conductivity of dielectric solids at elevated temperature is determined by phonon scattering by crystal imperfections and other phonons. Oxide pyrochlore compounds exhibit many of the features associated with low thermal conductivity materials. The pyrochlore crystal structure has a high intrinsic defect concentration. It has been experimentally established that as the difference in atomic mass between constituents in a compound increases, the thermal conductivity ofthat compound tends to decrease. Although the pyrochlore and fluorite structure are closely related, substitution of a high concentration of high atomic mass atoms (lanthanum, gadolinium and yttrium) into the fluorite structure provides a means to lower thermal conductivity that does not readily exist with stabilized zirconia compounds. It should be noted that, for thermal barrier applications, the benefits obtained from the reduction in thermal conductivity resulting from the use of high atomic mass elements must out weigh the debit incurred from higher density.

Reduction in thermal conductivity has also been associated with increasing complexity of crystallographic structure. As shown in Fig. 1a, the pyrochlore structure exhibits a greater degree of complexity than the fluorite structure shown in Fig. 1b. The cubic pyrochlore structure is similar to the cubic fluorite structure but with a large number of the oxygen atoms displaced (and one in eight missing).

Thermal barrier coatings are typically applied by thermal spray processes, such as plasma spray, in air (APS) or in low pressure (LPPS) by high velocity oxygen fuel processes (HVOF) or by detonation guns (D Gun). Electron beam physical vapor deposition (EBPVD) and sputtering are other techniques. Electron beam physical vapor deposition is a favored process. Depending upon the application and circumstances, each process has particular advantages. All ofthese processes can be readily used to apply oxide pyrochlore thermal barrier coatings. As previously discussed, the EBPVD process offers advantages since it develops a structure suited for extreme temperature applications and is therefore be most suitable for coating hot section turbine components. Thermal spray processing offers advantages in coating large components of complex shape and would be most suitable in coating components such as combustors.

Figs. 3a, b and c illustrates variants of the thermal barrier coatings of the present invention. Fig. 3a depicts a coated article which comprises a superalloy substrate 10 having a pyrochlore top coat 20 on its outer surface 21. In gas turbine applications the backside 11 of the superalloy substrate 10 will be cooled by cooling air (not shown) and the outside front surface 21 of the pyrochlore will be exposed to elevated temperatures. There may also be holes between the outer surface and the backside permitting cooling air to flow from the backside to the outer surface. Angled and shaped cooling holes in combination with flowing hot gases on the outer surface can produce film cooling in which a layer of cool air separates the outside surface from the hot gases to further reduce heat flow. Heat will flow from the front surface 21 to the cooled surface 11 and the quantity of the heat flow will be substantially reduced by the pyrochlore layer. As previously mentioned the pyrochlore may be applied by various methods and the macrostructure of the pyrochlore layer will be largely a function of the deposition process. The most basic invention embodiment is a pyrochlore layer adhered to a substrate which reduces heat flow in the presence of a thermal gradient.

Fig. 3b illustrates a preferred construction which employs a bond coat 15 between the substrate 10 and the pyrochlore 20. The bond coat 15 improves adherence and provides oxidation protection for the substrate. Fig. 3c is an expanded view of the interlayer 16 between the bond coat 15 and the pyrochlore layer 20. An oxide layer 22, principally of alumina, exists at this interlayer and is believed to be principally responsible for the adherence of the pyrochlore.

It is known to augment the naturally occurring alumina layer on the bond coat by sputtering alumina onto the bond coat, in the case of zirconia thermal barrier coatings, and the use of a separately applied alumina layer (rather than a thermally grown oxide layer) is also an embodiment of this invention.

In a further embodiment another ceramic layer may be applied to the free surface of the pyrochlore. This added layer can be selected to reduce oxygen diffusion, to provide erosion and abrasion resistance, or to provide a desired thermal emissivity characteristic, or some combination of these characteristics.

Example I

The use of the $La_2Zr_2O_7$ (lanthanum zirconate) pyrochlore oxide compound as a EBPVD applied thermal barrier coating will be illustrated. The advantageous properties of the $La_2Zr_2O_7$ pyrochlore oxide relative to stabilized zirconia for thermal barrier coating include thermal conductivity, thermal expansion, density, and phase stability. Fig. 4 shows the La_20_3 - $Zr0_2$ phase diagram with the pyrochlore phase field labeled P. It can be seen that the pyrochlore structure (at about 35 mol % La_20_3) is stable up to the melting point at about 2300 °C (4172 °F).

Fig. 5 shows thermal conductivity of $La_2Zr_2O_7$ compared to the thermal conductivity of cubic zirconia as a function oftemperature. At typical thermal barrier coating use temperatures, the pyrochlore compound exhibits a thermal conductivity which is about 50% that of stabilized zirconia. The density of the $La_2Zr_2O_7$ pyrochlore compound is approximately the same as stabilized zirconia (approximately 6gr/cm^3) so on a weight corrected basis, the thermal conductivity benefit is also about 50%.

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To illustrate the benefit, the 50 percent reduction thermal conductivity allows the coating thickness to be reduced by 50 percent for the same degree of thermal protection. Decreasing the coating mass by 50 percent on a typical turbine blade will lower the blade pull at the blade root by approximately 1,500 pounds (680 Kg), at typical operating conditions, which results in a significant increase in blade life and permits a reduction in mass of the disk to which the blades are attached. If the thermal barrier coating were held at the same thickness, and the cooling air flow held constant, the substrate temperature would be reduced by about 100 °F (55 °C), giving increased substrate creep life. Keeping the coating thickness constant and reducing the airflow would increase engine efficiency.

Fig. 6 shows the mean coefficient of thermal expansion of $La_2Zr_2O_7$ compared to that of cubic stabilized zirconia as a function oftemperature. The thermal expansion of $La_2Zr_2O_7$ thermal barrier coating can be seen to be similar to that ofthe cubic zirconia thermal barrier coating. This means that $La_2Zr_2O_7$ will behave similarly to zirconia during thermal cycling.

Example II

Lanthanum zirconate was applied to a substrate by electron beam vapor deposition (EBPVD), in a controlled atmosphere chamber. The coating was applied to a single crystal substrate (ofthe nominal composition of PWA 1480 (see Table II)). The coating process was carried out in a vacuum of 3.2×10^{-4} Torr (4.3×10^{-2} Pa) with an oxygen flow rate of 50 sccm (8.33×10^{-7} m^3/s at specified standard temperature and pressure). Oxygen was added to ensure pyrochlore oxygen stoichiometry, see U.S. Patent 5,087,477. The substrate temperature was 1840°F (1005°C) during deposition with a substrate to source distance of 5.25 inches (135mm). The source pyrochlore ceramic was evaporated with an electron beam run at 0.8 A and 10,000 V. The source oxide was $La_2Zr_2O_7$ powder. The coating exhibited the favorable columnar grain structure typical of electron beam physical vapor deposited cubic zirconia thermal barrier coatings that provides strain relief and improved durability over plasma sprayed coatings.

Fig. 7 shows an X-ray diffraction scan obtained from the surface of the coating. The diffraction peaks have been indexed to the pyrochlore crystal structure which demonstrates that the pyrochlore structure was formed in the deposited thermal barrier coating.

Claims

1. A metallic article comprising a metallic substrate (10), said substrate having a ceramic coating (20) wherein said ceramic coating has a cubic pyrochlore structure.

2. A method of thermally insulating a metallic substrate (10) which comprises applying a cubic pyrochlore ceramic coating (20) to at least a portion of said substrate by electron beam physical vapor deposition or thermal spray deposition.

3. An article as claimed in claim 1 or a method as claimed in claim 2, wherein said metallic article has an oxide scale on its outer surface, said oxide consisting substantially of alumina, and wherein said pyrochlore ceramic coating (20) is bonded to said oxide scale.

4. A metallic article comprising a metallic substrate (10), said substrate having an alumina forming coating (15) on its surface and a pyrochlore coating (20) bonded to said alumina forming coating.

5. An article as claimed in claim 4, wherein said substrate coating (20) comprises an alumina forming metallic overlay coating.

6. An article as claimed in claim 4, wherein said substrate coating (20) comprises a diffusion aluminide coating.

7. An article as claimed in any of claims 1 or 3 to 6, or a method as claimed in claim 2 or 3, wherein said metallic substrate (10) is selected from the group consisting of steels, superalloys, titanium alloys and copper alloys.

8. An article as claimed in any of claims 1 or 3 to 7, or a method as claimed in claims 2, 3 or 7, wherein said pyrochlore has the formulae $A_2B_2O_7$, $A_2B_2O_6$ or AB_2O_6.

9. An article or method as claimed in claim 8, wherein said pyrochlore has the formula $A_2B_2O_7$ and the A and B species ionic radii fall approximately within the cubic field in Fig. 2.

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10. An article as claimed in any of claims 1 or 3 to 9 or a method as claimed in any of claims 2, 3 or 7 to 9, wherein the B constituent comprises Hf, Ti, Zr, and single phase mixtures thereof.

11. An article as claimed in any of claims 1 or 3 to 10 or a method as claimed in any of claims 2, 3 or 7 to 10, wherein the A constituent comprises La, Gd, Y, and single phase mixtures thereof.

12. An article as claimed in any of claims 1 or 3 to 11, or a method as claimed in any of claims 2, 3 or 7 to 11, wherein said coated article is adapted to be used in environments where the free surface (21) of the pyrochlore coating (20) will be heated and the free surface (11) of the substrate (10) will be cooled, whereby the pyrochlore coating will reduce heat flow.

13. An article as claimed in any of claims 1 or 3 to 12, or a method as claimed in any of claims 2, 3 or 7 to 12, wherein said pyrochlore has a columnar microstructure.

14. A superalloy gas turbine component (10) which operates in a environment with gas temperatures in excess of 1,000°c, said component having internal cooling passages, wherein said component comprises a coating (20) of a ceramic having a pyrochlore crystal structure, said coating being located to reduce heat flow into said component.

15. A gas turbine engine component which comprises a superalloy substrate (10) having a layer consisting substantially of lanthanum zirconate on at least a portion of its external surface.

16. The use of a ceramic coating having a pyrochlore structure as a thermal barrier coating.

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FIG.1A

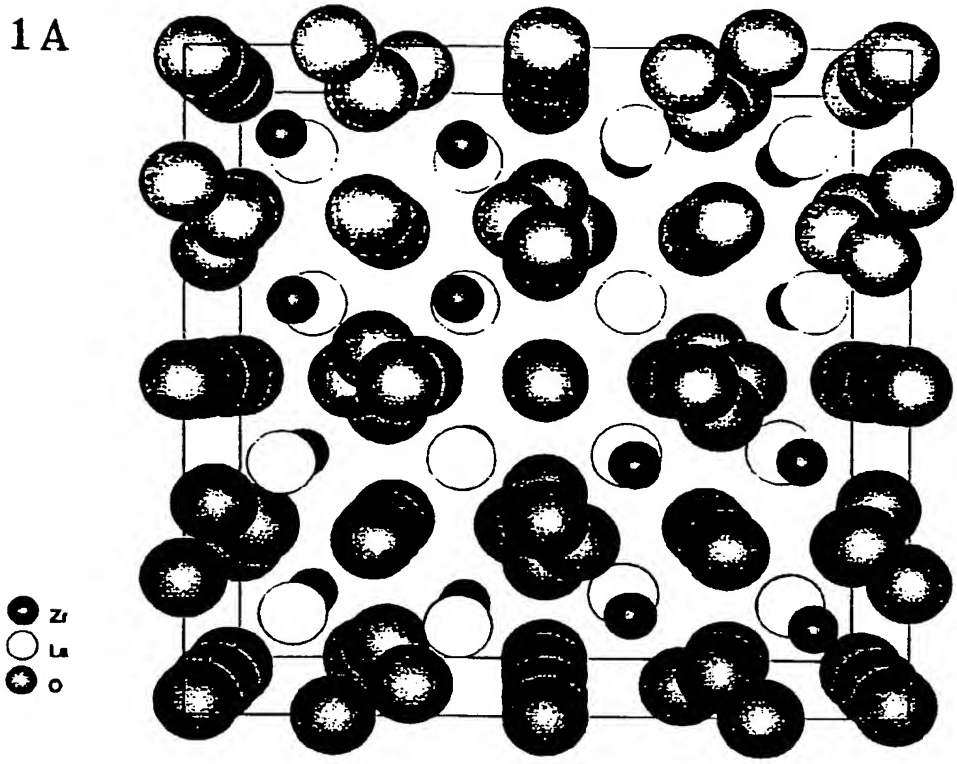
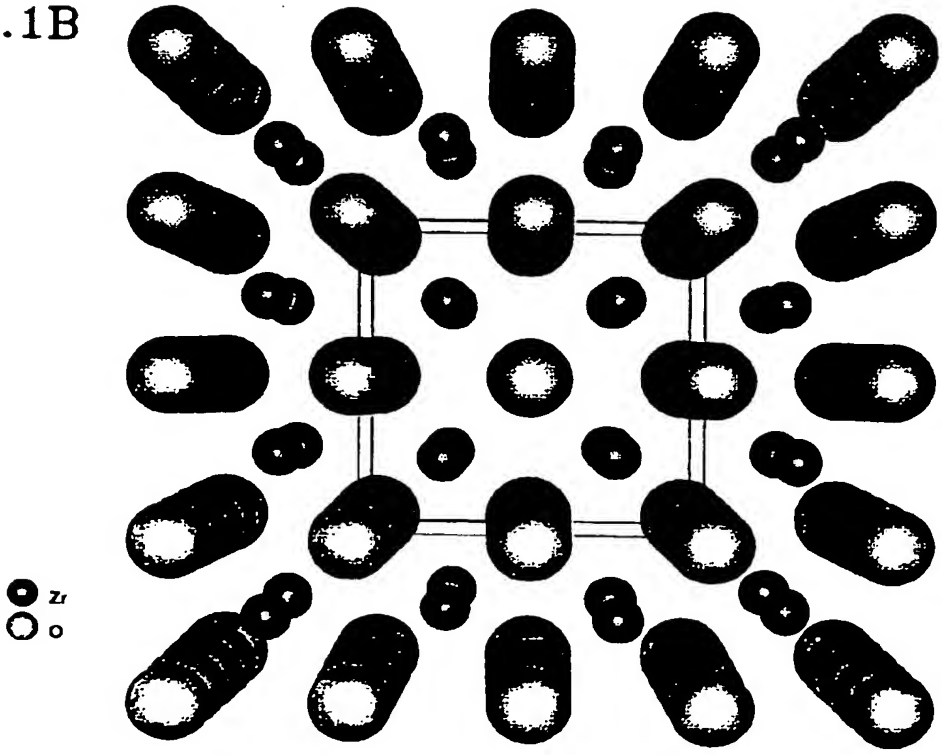


FIG.1B



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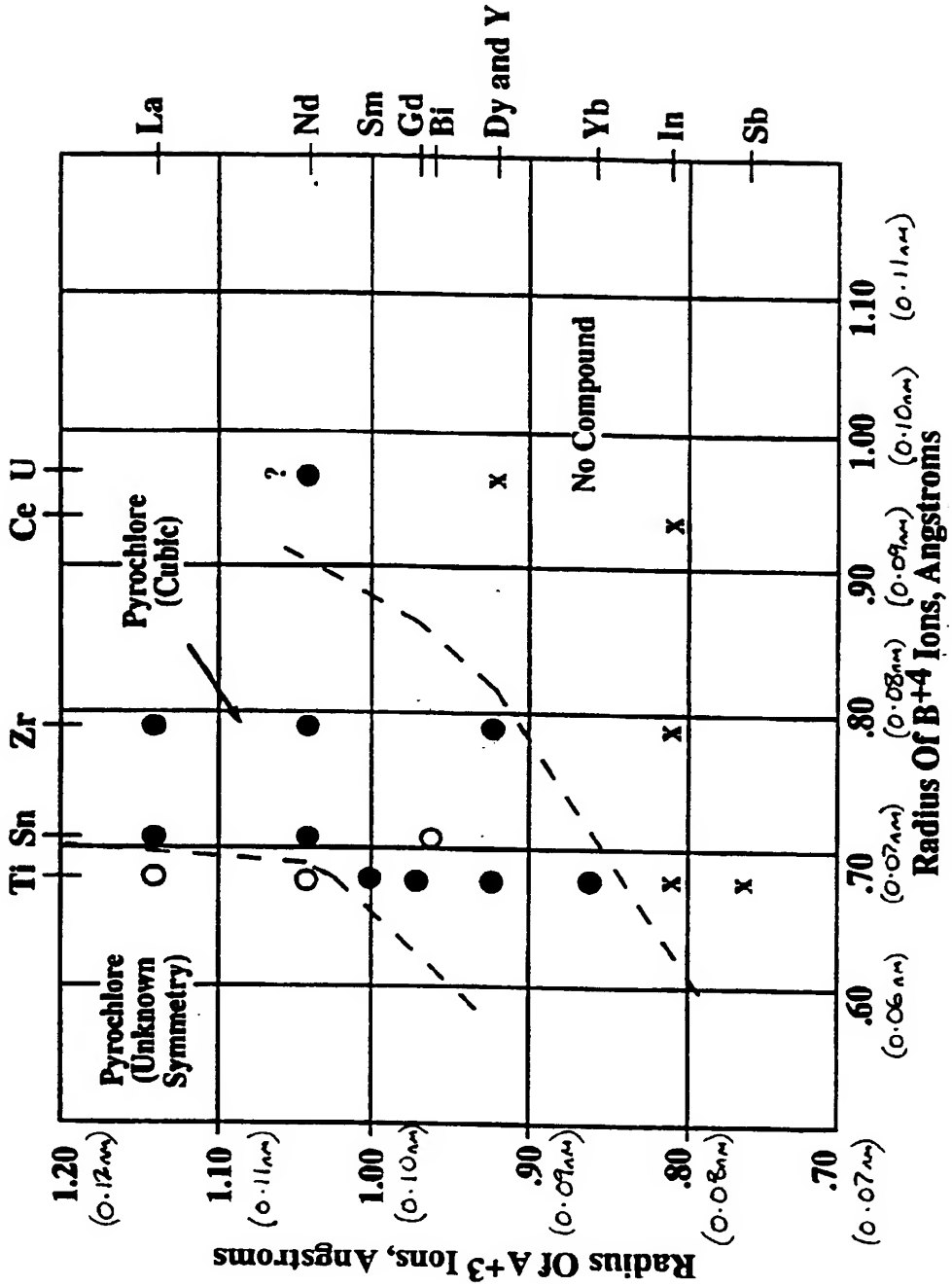

FIG.2

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FIG.3A

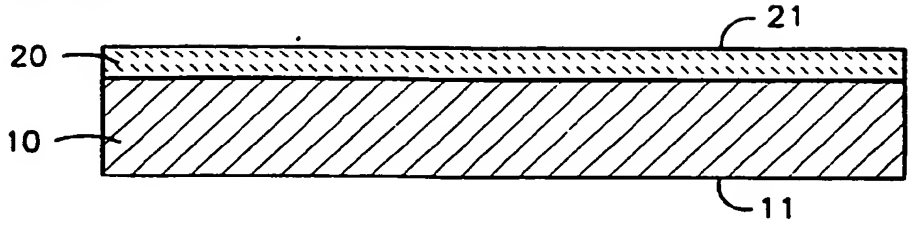
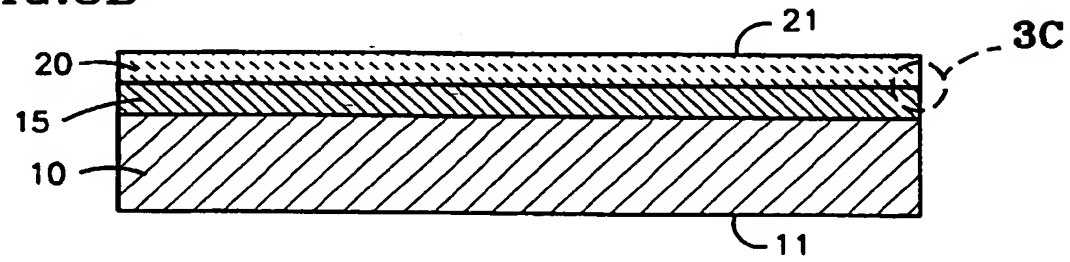


FIG.3B



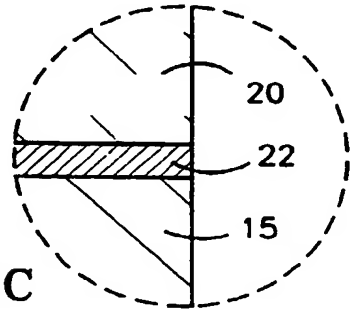


FIG.3C

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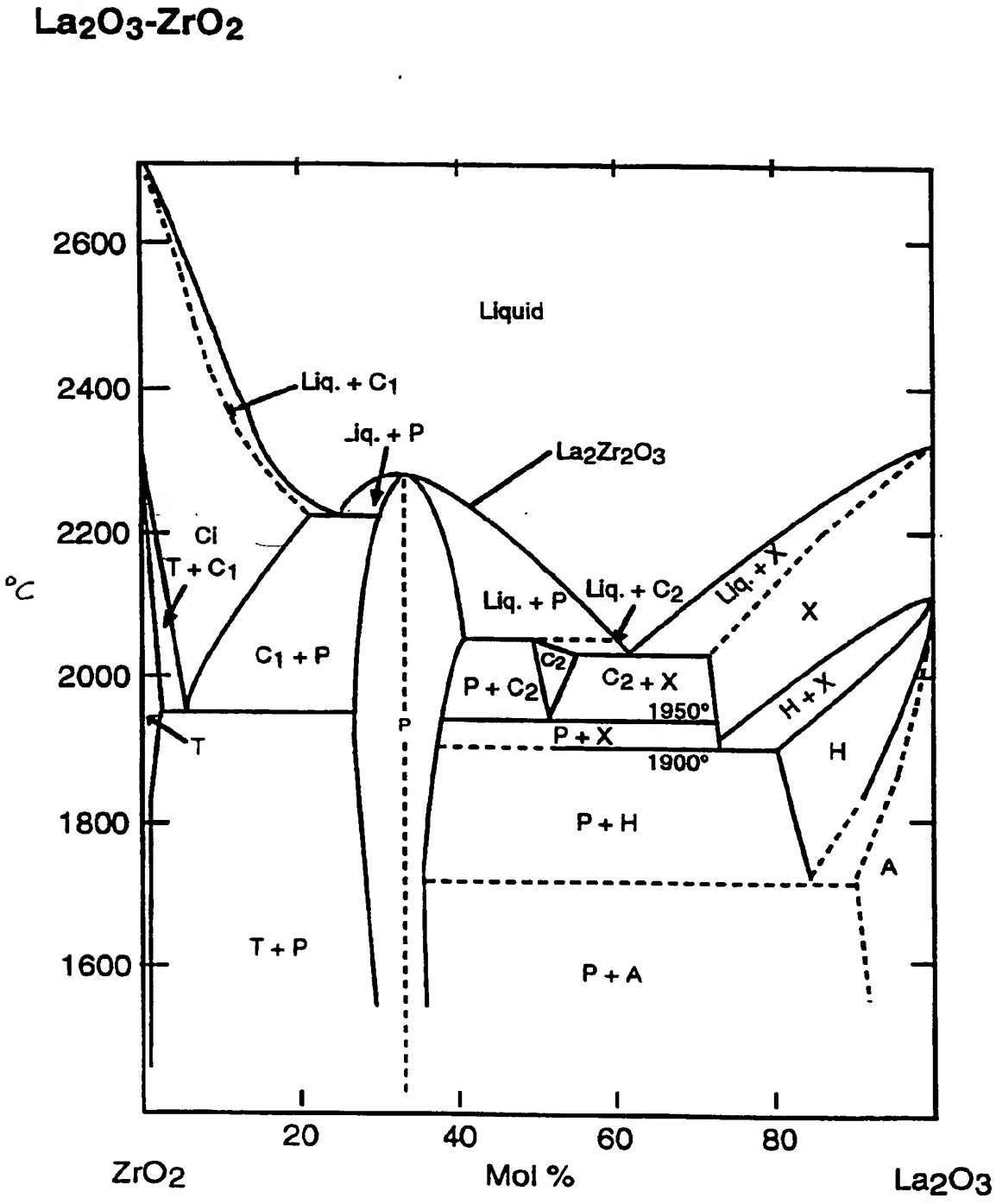
FIG.4



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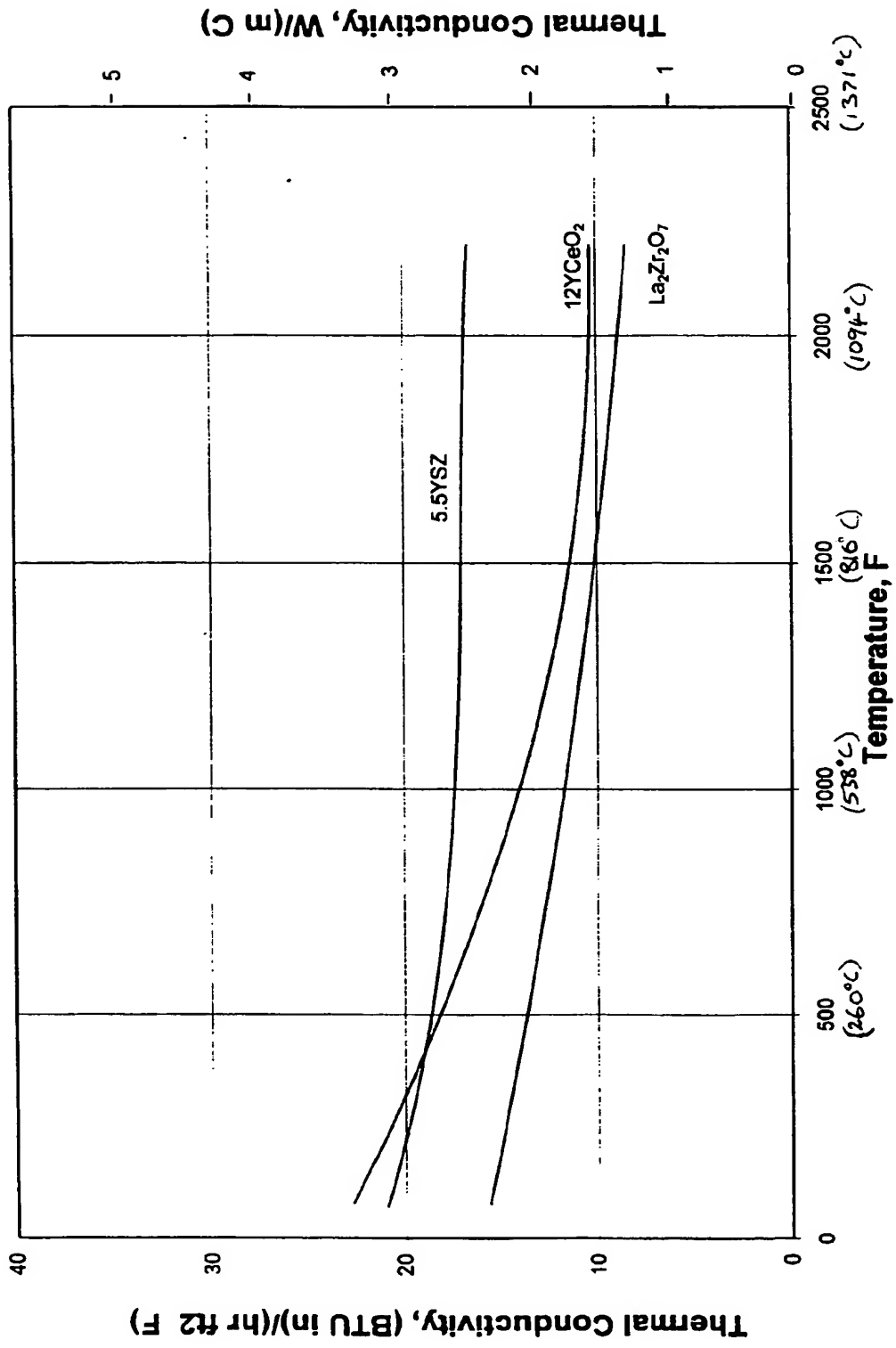

FIG.5

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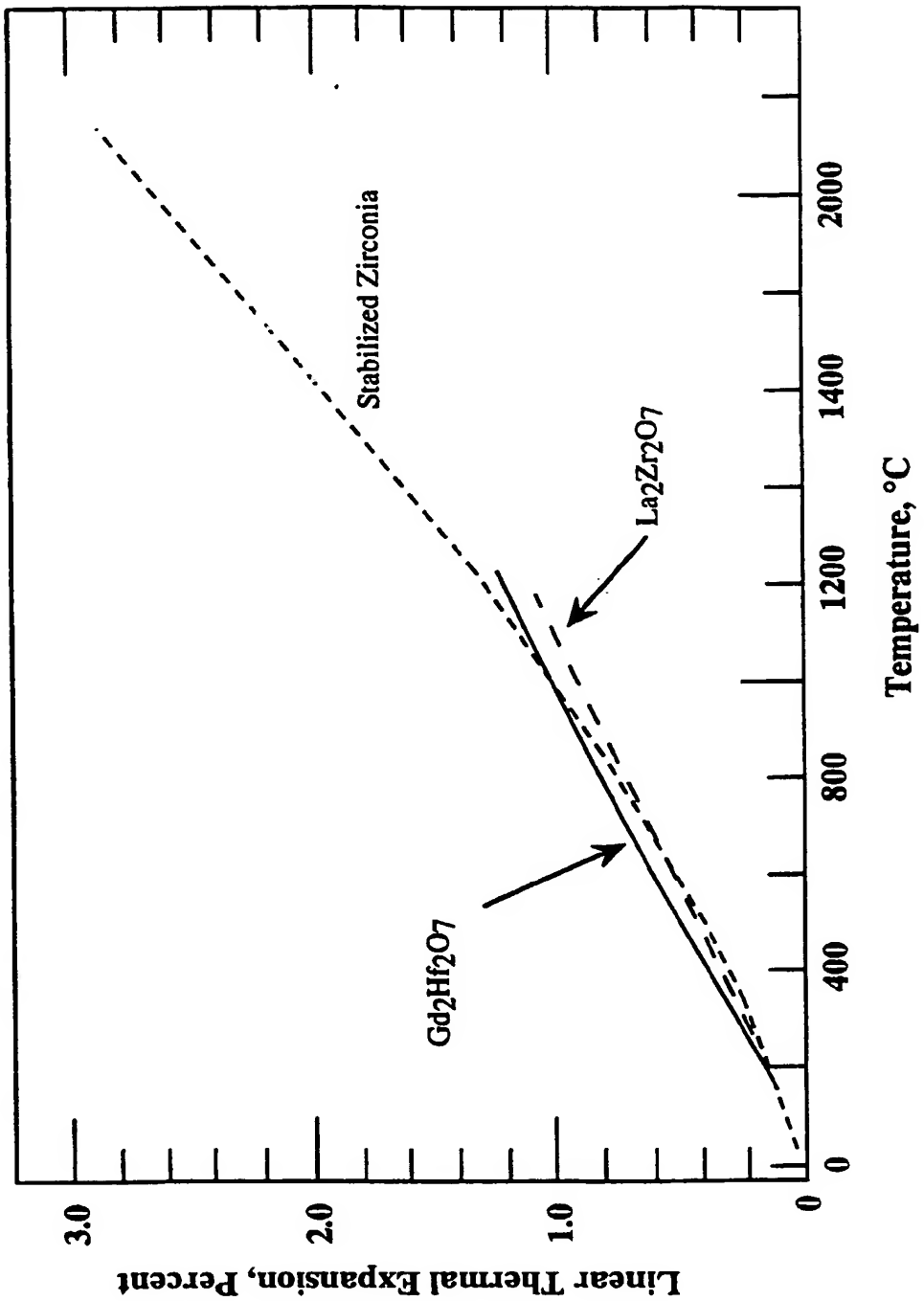

FIG.6

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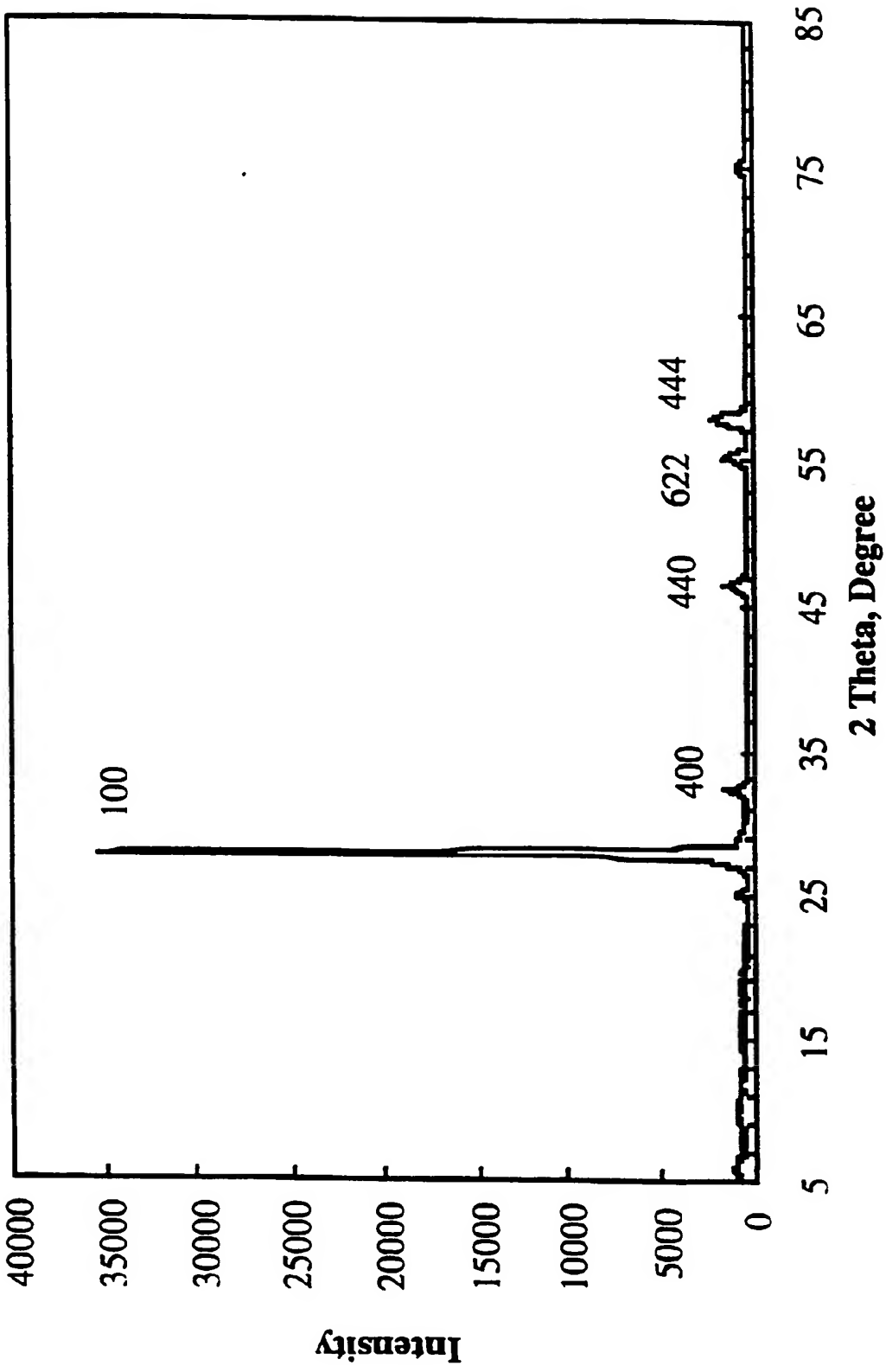
FIG.7



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EUROPEAN SEARCH REPORT

Application Number EP 97310056.3

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 6)
A	Derwent Accession on Questel, week 9109, London: Derwent Publications Ltd., AN 91-063347, Class C25D; & JP 3-13599 A (NIPPON STEEL CORP.). --	1-16	C 23 C 4/10 F 02 C 7/00
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A	US 3954512 A (KANTER) 04 May 1976 (04.05.76), the whole document. ----	1-16	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 6) C 23 C F 02 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	23-03-1998	BECK

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